# Surface Morphology Investigation during In-situ CdS Nanoparticles Growth in Hybrid P3HT:SA Films via Gas Exposure Technique

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The unique physical features of group II-VI inorganic semiconductor nanoparticles, including their high surface area and nanoscale size, have attracted significant study interest. When these nanoparticles are integrated with organic semiconductor materials, they form multifunctional materials with advantageous features for usage in electronic devices. This study prepared organic/inorganic thin films by depositing P3HT, stearic acid (SA), and $Cd^{2+}$ ions onto silicon substrates by a novel Angle Lifting Deposition (ALD) technique. The films were then exposed to $H_2S$ gas for 2, 4, 6, and 15 h to nucleate CdS nanoparticles within the P3HT:SA matrices. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX) were used to characterize the hybrid organic/inorganic thin films. Both morphological and elemental studies demonstrated the existence of CdS nanoparticles. The optimized gas exposure time for hybrid polymer P3HT:SA:CdS was 6 h. This study implies that ALD and gas exposure techniques are practical for fabricating hybrid organic/inorganic nanocomposite thin films at room temperature.

Keywords: CdS nanoparticles, P3HT, Stearic acid, $H_2S$ gas, FESEM, EDX.

## 1. INTRODUCTION

The demand for thin films has led to numerous thin-film deposition techniques based on the material compatibility and substrate sizes employed in various applications. In general, thin films can be deposited on substrates by two methods: physical and chemical. The physical vapour deposition (PVD) method can be divided into evaporation and sputtering. Chemical methods include chemical vapour deposition (CVD), spin coating, dip coating, and Langmuir-Blodgett (LB) [1].

The LB method does not require high temperatures or a vacuum environment. It can be used to deposit a flat and smooth organic thin film without damaging the substrate surface. In addition, with molecular layers, the arrangement of molecules is more structured and stable [2]. These features, along with the use of little organic material, require only a few microliters of material solution, which garnered attention to this work. However, the LB method deposition procedure takes a long time to complete. A new thin-film deposition technique known as Angle Lifting Deposition (ALD) was developed in this study to accelerate the deposition time. ALD is a modification of the LB technique, in which the film is deposited at a 45-degree angle.

Due to their wide range of possible applications in modified electrodes [3], batteries [4], and solar devices [5], extremely thin and highly structured organic-inorganic films built on solid substrates have garnered considerable attention in recent decades. Layer-by-layer structural ordering is beneficial for enhancing charge carrier mobility [6].

In hybrid organic-inorganic thin films, inorganic semiconductor nanoparticles act as electron acceptors [7]. CdS, CdSe, ZnO TiO$_2$, PbS, PbSe, and CdTe are examples of frequently used nanoparticles [9] that are of high quality and have great demand in the research and development of modern solar photovoltaic cells.

## 2. EXPERIMENTAL TECHNIQUE

### 2.1 Materials

P3HT polymer was chosen as the primary material in this investigation due to its many advantages. P3HT derived from polythiophene is a good material with a low cost, high electrical conductivity, and excellent optical properties. P3HT exhibits a high charge carrier mobility (typical hole mobility) of $10^{-4}$ to $10^{-1}$ cm$^{-2}$/Vs [10], a low band-gap energy of $\sim 1.9$ eV [11] and good self-organization capability. It is insoluble in water but fairly soluble in chloroform. However, P3HT is a non-amphiphilic substance, making it incompatible with standard LB deposition. When spread on the water surface, P3HT aggregates into three-dimensional structures to decrease polymer-water contact or interaction [6].

Cadmium chloride (CdCl$_2$) was used in this study as a platform for supplying Cd ions. The dissolution of CdCl$_2$ in water yields $Cd^{2+}$ and $2Cl^-$ ions. Chemically, $Cd^{2+}$ ions will bind to SA and P3HT, but chloride (Cl$^-$) ions will dissolve in DI water in the Langmuir trough. Since CdCl$_2$ decomposes in water and P3HT is unable to trap $Cd^{2+}$ ions immersed in water, a ligand is required. Stearic acid (SA) was used as $Cd^{2+}$ ions ligand for P3HT in this work. SA, which is classified as a fatty acid, can lessen the dominance of the hydrophobic part of P3HT. SA enhances the stability of polymer and decreases the chance of the creation of super monolayer structures [12].

Furthermore, SA aids in the P3HT dispersion process by reducing the cohesive forces [13]. SA is frequently used in daily living, such as bath soap and laundry soap. SA is a hydrogen-filled saturated fatty acid, and most saturated fatty acids have a linear hydrocarbon bond structure. SA is amphiphilic, in which the long component of the hydrocarbon (CH) bond is insoluble in

water, while the free portion of COOH is soluble in water and traps $Cd^{2+}$ ions that are present in water. SA tends to form a monolayer on the surface of the water.

### 2.2 Device Fabrication

The floating P3HT:SA monolayer was initially deposited on the substrate using the standard LB method, but the results were unsatisfactory. This is due to the long-bond molecular weight of the P3HT polymer. A new technique known as ALD was devised to address this issue, as depicted in Fig. 1. The ALD method allows the deposition of thin films on a large substrate, and the polymer arrangement can also be tweaked [14].
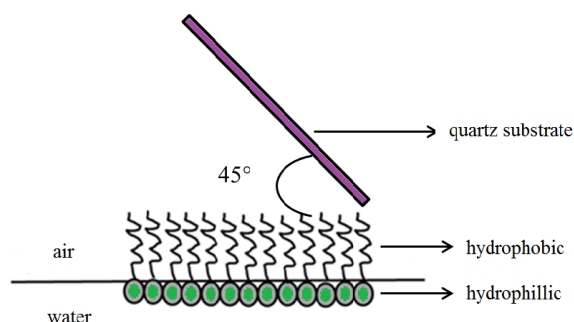


**Fig. 1** – ALD technique

The ALD technique was developed based on the LB method. This new deposition technique was performed using the KSV 2002 System 2 instrument. The cleanliness of equipment such as hydrophobic troughs and barriers is critical in assuring the quality of thin film production. The trough was wiped using $CHCl_3$ solution and rinsed with DI water. Following the completion of the trough cleaning, the barrier was cleaned using the same approach, but this time with an ethanol solution.

P3HT:SA:$Cd^{2+}$ thin films were obtained when 400 µl of P3HT in chloroform were spread on 0.5 mM of $CdCl_2$ subphase. Immediately after, the capping agent, SA in chloroform, was disseminated (100 µl). Thin film samples were deposited on a silicon substrate using the ALD technique. The deposition angle was 45°, while the surface pressure of P3HT and SA was kept consistently at 27 mN/m.

These samples were then exposed to $H_2S$ gas in a closed glass chamber for 2, 4, 6, and 15 h by mixing hydrochloric acid with iron (II) sulfide (FeS). The chemical reaction between the two is shown below:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S .$$
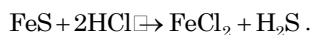
When subjected to the gas, $S^{2-}$ ions reacted with $Cd^{2+}$ ions trapped by SA, causing the CdS nanoparticle to grow. The samples were then heated at 80 °C for 10 mins. Heating (annealing) can enhance crystal structure, reduce porosity, and eliminate solvent residue left behind from thin film deposition. [15]. Finally, thin film samples were morphologically and elementally analyzed.

### 2.3 Characterisation

The morphological and elemental characterization was performed using the Hitachi model SU 8020 UHR-del FESEM to determine the shape and diameter size of CdS nanoparticles formed in P3HT matrices. In addition, the surface condition of the formed films can also be seen through this microscope. Upon obtaining the image from FESEM, the sample was further characterized using EDX analysis to determine the element content present in the samples and its percentage. The characterisation findings are presented in several formats, including graphs and tables that indicate the element's presence and proportion.

## 3. RESULTS AND DISCUSSION

### 3.1 Surface Morphology

Fig. 2 shows images of pristine P3HT and P3HT:SA:$Cd^{2+}$ thin films. Fig. 2a depicts P3HT molecules with an ordered cloud structure, and no form of nanoparticles can be observed between the matrices or interstices of P3HT molecules. Fig. 2b depicts P3HT:SA:$Cd^{2+}$ with more significant polymer clouds. Because of their small size, SA molecules are imperceptible. However, these SA molecules surround P3HT molecules, capping cadmium ions and causing the polymer structure to rearrange.
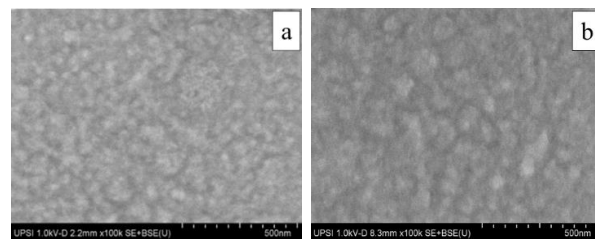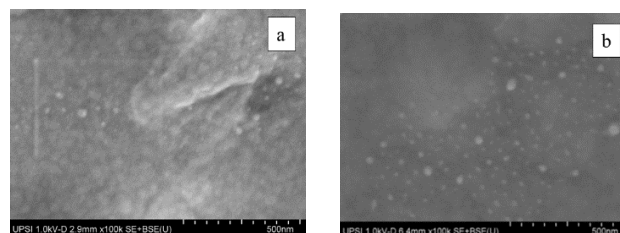


**Fig. 2** – FESEM images for thin film samples: (a) P3HT, (b) P3HT:SA:$Cd^{2+}$

Fig. 3 depicts the existence of CdS nanoparticles after the sample has been exposed to sulfide gas ($H_2S$). The increment of exposure time causes the number of nanoparticles to increase; hence the distance between neighbouring nanoparticles decreases. The volume fraction, size, and dispersity of nanoparticles profoundly affect the characteristics of thin films [16]. The images show that the quantity of CdS nanoparticles in the samples increased with increasing exposure period, except at the 15-hour exposure time. The majority of $Cd^{2+}$ ions are believed to combine with $S^{2-}$ ions on the thiophene ring after exposure of the sample for 15 h [17]. It can be seen that the amount of CdS nanoparticles in the sample exposed for 6 h was the highest when compared to the other samples.

Overall, the optimal exposure time for the study was 6 h. All obtained images showed that the size of nanoparticles was confined between 13 and 20 nm and did not increase. This was due to the fact that the nanoparticles were capped inside the P3HT matrices.
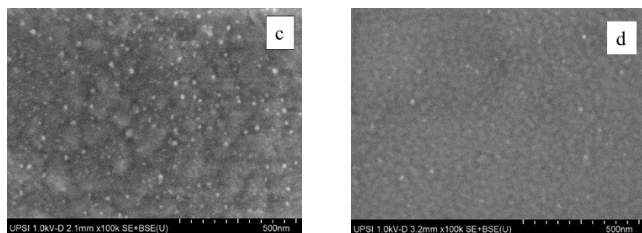
**Fig. 3** – FESEM images of thin film samples after P3HT:SA: $Cd^{2+}$ exposed to $H_2S$ for: (a) 2 h, (b) 4 h, (c) 6 h, and (d) 15 h

The proliferation of these nanoparticles can be observed in greater detail using EDX analysis. This finding is substantial because the size of nanoparticles determines their effectiveness in electronic applications, for example, in the active layer of solar cells. The study discovered that smaller nanoparticles are more beneficial when incorporated within the active layer, whereas larger nanoparticles are more effective when included outside the active layer [18].

### 3.2 EDX Analysis

As can be seen in Fig. 4, apart from Carbon (C), Hydrogen (H), and Silicon (Si) elements, Cadmium (Cd) and Sulfur (S) elements were also detected by the EDX instrument in samples exposed to $H_2S$ gas.
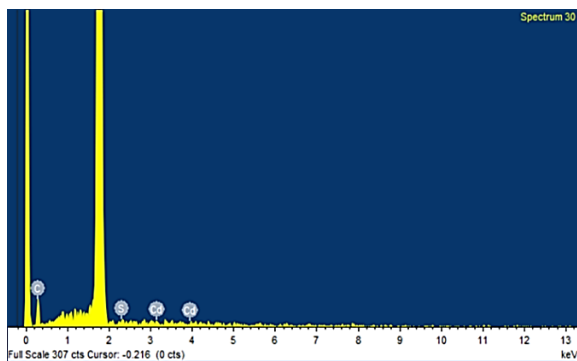


**Fig. 4** – Sulfur (S) and Cadmium (Cd) elements detected by EDX in the sample after exposure to $H_2S$ gas

The elemental data from EDX analysis for samples before and after gas exposure were then collated in a table for a more explicit comparison. Table 1 shows the percentage of elements present in the sample before and after exposure to $H_2S$ gas. O, H, and Si elements are not counted since we are only interested in Cd and S. The percentage of Si elements is high because the substrate used is silicon. In contrast, O and H are the building blocks of organic materials [19]. As seen in Table 1, the proportion of element S rose as the duration of gas exposure increased. It demonstrates that the sample exposed for 6 h contained the greatest concentration of sulfur, 8.33 %. In addition, as depicted by the graph in Fig. 5, when the sample was exposed for longer than 6 h, the percentage of S element in the sample tended to decrease. These findings are consistent with the results obtained in the characterization of FESEM, as illustrated earlier in Fig. 2 and Fig. 3, where at 6 h, the creation of nanoparticles can be seen in comparison

to others. This is due to the reaction of $S^{2-}$ and $Cd^{2+}$ ions having achieved its optimal exposure time of 6 h.

**Table 1** – Elemental percentage in the samples before and after exposure to $H_2S$ gas

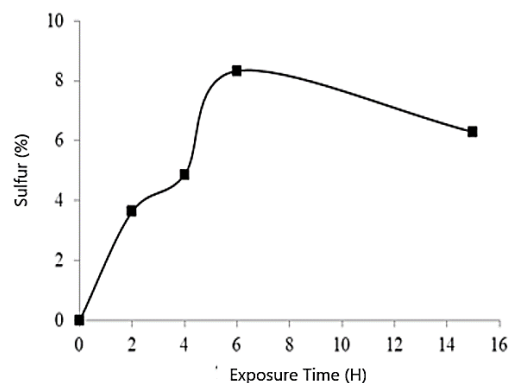| Sample | Exposure time (hours) | C (%) | Cd (%) | S (%) |
|---|---|---|---|---|
| P3HT:SA:$Cd^{2+}$ | 0 | 88.62 | 9.69 | 1.69 |
| P3HT:SA:CdS | 2 | 86.61 | 9.77 | 3.63 |
| | 4 | 85.58 | 9.55 | 4.87 |
| | 6 | 82.37 | 9.30 | 8.33 |
| | 15 | 83.99 | 9.73 | 6.29 |



**Fig. 5** – Percentage of element S present in P3HT:SA:CdS (after exposure to $H_2S$ gas)

## 4. CONCLUSIONS

A simple gas exposure method has been studied to nucleate CdS nanoparticles inside semiconductor polymer (P3HT) matrices at room temperature. The technique eliminates the need for numerous chemical and time-consuming processes in the present method of producing a thin film. The longer gas exposure duration does not necessarily result in a more significant amount of formed nanoparticles. According to this study, the optimal exposure duration for nucleating CdS between P3HT matrices is 6 h. FESEM and EDX analyses verified the presence of nanoparticles with diameters of 13 to 20 nm. Since the matrix used in this study is P3HT, it faced several problems because polymers typically form unstable stacked polymers at the air/water interface, making it extremely challenging to transfer the film to a solid substrate using the standard LB method. However, the ALD technique allows the polymeric film to be deposited on a large-scale substrate. This study's findings can also be used in the future to assess the reliability of hybrid nanocomposite thin films created using the ALD process.

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## Дослідження морфології поверхні під час in-situ вирощування наночастинок CdS в гібридних плівках P3HT:SA за допомогою методу впливу газу

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Унікальні фізичні властивості наночастинок неорганічних напівпровідників груп II-VI, включаючи їхню високу площу поверхні та нанорозмір, привернули значний дослідницький інтерес. У процесі інтегрування наночастинок з органічними напівпровідниковими матеріалами, вони утворюють багатофункціональні матеріали з перевагами для використання в електронних пристроях. При проведенні даного дослідження були підготовлені органічні/неорганічні тонкі плівки шляхом нанесення іонів P3HT, стеаринової кислоти (SA) та $Cd^{2+}$ на кремнієві підкладки за новою технікою кутового осадження (ALD). Потім плівки піддавали впливу газу $H_2S$ протягом 2, 4, 6 і 15 годин для утворення зародків наночастинок CdS в матрицях P3HT:SA. Для характеристики гібридних органічних/неорганічних тонких плівок використовували автоелектронну скануючу мікроскопію (FESEM) і енергодисперсійне рентгенівське випромінювання (EDX). Як морфологічне, так і елементне дослідження продемонстрували існування наночастинок CdS. Оптимізований час впливу газу для гібридного полімеру P3HT:SA:CdS становив 6 год. Проведене дослідження означає, що методи ALD і впливу газу практичні для виготовлення гібридних органічних/неорганічних нанокомпозитних тонких плівок при кімнатній температурі.

**Ключові слова:** Наночастинки CdS, P3HT, Стеаринова кислота, Газ $H_2S$, FESEM, EDX.